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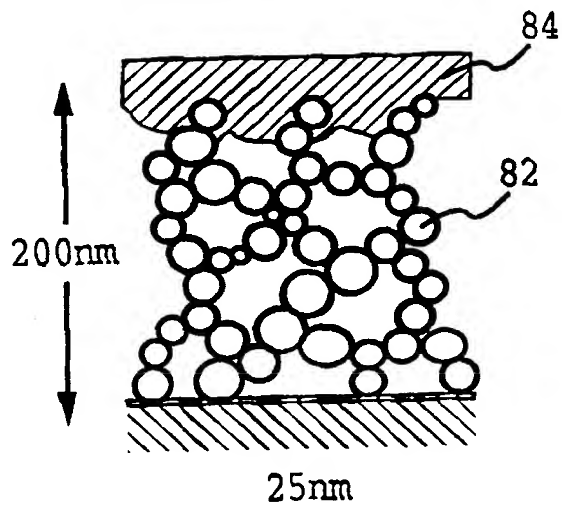
(54) Title: LOW DENSITY FILM FOR LOW DIELECTRIC CONSTANT APPLICATIONS

(57) Abstract

A film having a dielectric constant of less than 3 (most preferably less than 2) and comprising a layer of particles and a deposit on top of and within the particle layer, and a method of making same. The particles are agglomerated particles, hollow particles, porous particles, or a combination thereof. The film is substantially planar on its surface, and the film is substantially impermeable to gases. The method comprises coating a substrate with the particles (preferably spin-coating a colloidal solution); drying the particles to form a substantially uniform particle layer; depositing a deposit onto the particle layer (preferably by low pressure chemical vapor deposition and causing chemical vapor infiltration to bond the particles to the substrate); and optionally polishing/planarizing the deposit surface (preferably by chemical mechanical polishing).



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LOW DENSITY FILM FOR LOW DIELECTRIC CONSTANT APPLICATIONS

BACKGROUND OF THE INVENTION

Field of the Invention (Technical Field):

The present invention relates to porous thin films, especially those employed as an electrical insulator, and most especially in integrated circuit applications.

Background Art:

A chief manner in which to improve the speed of integrated circuits is to reduce transistors in size so that their density is increased. The metal interconnects between the transistors and the insulating layers separating the interconnects also must be reduced in size. This shrinkage of features causes increased delays in transmission of information amongst the components because of increased impedance in the interconnect and crosstalk through the interlayer dielectric material (ILD). If the dielectric constant of the ILD material could be decreased, then the problem of crosstalk could be diminished. Thus there is a need for an ILD material that has better characteristics than the current material, dense SiO_2.

Multichip Modules (MCM) are ceramic- and organic-based structures (boards) onto which components such as resistors, transistors, varistors, capacitors, integrated circuits, and the like, are mounted to form circuit boards. These MCMs have a wide variety of applications in virtually every electronic device including cell phones, camcorders, computers, and displays. Several technologies exist for the fabrication of MCMs. In ceramic-based MCMs, the MCM is produced from ceramic powders that are combined into structures with metal powders and then heated to fuse the particles together. In the organic-based approach (printed wiring board laminates), layers of polymer (often epoxy) are combined with metal structures formed by electroless plating or evaporation/sputtering to form the MCM.

In the future, MCMs are expected to deliver higher performance which requires operation at higher frequencies. These higher frequencies require lower dielectric constants over a wide frequency band into the gigahertz region. An approach that has been developed to lower the dielectric constant of both organic (polymer) and ceramic-based MCMs is to add hollow microspheres to the substrate material (MCM) thereby lowering the dielectric constant by adding

controlled porosity to the material. Thus, there is a need for approaches to take hollow particles with suitable characteristics and combine them with other ceramic and polymeric materials to fabricate MCMs.

A problem with the current methods of low-dielectric-constant MCM fabrication is that the hollow particles must be mixed in with other materials (polymer for organic-based and ceramic for inorganic-based MCMs) and then fabricated into MCMs. Hollow particles with suitable average size, spread of the size distribution, composition, permeability are needed for these applications and special processing approaches must be taken. The combination of these hollow particles with the other solid-particle materials typically results in MCMs with dielectric constants greater than those desired because the non-hollow components have relatively high dielectric constants. Thus there is a need for both a simpler process for MCM fabrication with hollow particles and a process that gives lower dielectric constants than existing approaches.

Research is being conducted to find suitable low-dielectric-constant films to fulfill these needs. Fig. 1 demonstrates that porous films are the long-term solution for interlayer dielectrics because they have the lowest dielectric constants. Because a gas-filled pore has a dielectric constant close to 1, ideally one would like to incorporate as high a volume fraction of porosity into the interlayer dielectric as possible. According to the Semiconductor Industry (SIA) Roadmap, the electronics industry requires films that can be made both easily and economically using a process with a low cost of ownership, but at the same time be reliable. Closed porosity (non-aerogel-derived) silica films provide an answer because industry is already familiar with the properties of SiO_2 and has much experience processing it. Also, it is compatible with the materials currently used in integrated circuits. The main problems with aerogels, which also have low dielectric constants, are that they have poor mechanical properties, absorb and desorb moisture due to a permeable microstructure, require unconventional processing steps, and have suspect reliability.

Low dielectric-constant materials, such as interlayer dielectric (ILD) and intermetal dielectric (IMD) materials, represent an important part of the overall makeup of integrated circuits and multi-chip module packaging devices. As microelectronic devices become more complex, multiple levels of metallization are becoming common (see Fig. 2). Fig. 2 is a cross-section of a typical prior-art logic device **10** with four levels of metallization. Components include passivation layer **12**, solder

pad **14**, first intermetal dielectric **16**, second intermetal dielectric **18**, third intermetal dielectric **20**, interlayer dielectric **22**, source/drain (doped Si) **24**, gate oxide **26**, Si **28**, doped polysilicon **30**, field oxide **32**, contact plug **34**, local interconnect **36**, via Plug **38**, transmission line **40**, adhesion/diffusion barrier layers **42**, global interconnect **44**, and alignment due to dual damascene patterning **46**. The dielectric materials occupy over 50% of the total volume. Interlayer dielectrics play an important role in a multilevel metal system by providing insulation between the various levels of metallization in the circuit. Rather than being passive elements, ILD films in fact play an active role in defining the reliability and performance of the microelectronic device. Because the market for microelectronic devices is many billions of dollars and is projected to expand significantly through the next 25 years, improvements in ILD materials will be leveraged tremendously in future devices. During the same period of time, the dimensions of ILDs will continue to shrink until a 0.03 μm minimum feature size is reached, to accommodate greater than 10 levels of wiring, by about 2020. At these dimensions, the use of current interconnect materials may not be possible due to inherent property limitations. Currently there is substantial interest in, and effort to find and produce, materials that can replace both Al and its alloys as interconnection materials, such as Cu, and SiO_2-based insulators as ILDs. However, improvements in the ILD are most important because a switch from Al to Cu for the interconnect will result in only a 50% increase in device performance, while the switch to low K (dielectric constant) dielectrics can enable a 400% improvement.

It is important that the mechanical properties, thermal stability, impermeability to moisture, resistance to Al or Cu diffusion, low dielectric loss, and breakdown strength of the ILD be compatible with either Cu or Al multilevel processing and provide reliable operation. Dense silica and F-doped silica are currently used as ILDs. Organic polymers and aerogels are possible low K alternatives but have many problems and uncertainties regarding their physical properties and their reliability in microelectronic devices as ILDs.

A variety of problems limit the use of polymers in ILDs. First, few organic polymers have the ability to withstand 400°C without decomposing, the highest temperature achieved during subsequent interconnection fabrication. In addition, polymers have a lower modulus than silica which limits their ability to suppress hillock formation and provide physical/mechanical protection of the interconnects. Furthermore, it is difficult to pattern polymers because they chemically interact

with the photoresists and solvents used. Also, global planarization of polymers is troublesome because the polymers are inert to chemical etching and they are too soft for mechanical abrasion without suffering severe damage. Finally, spin-coating of polymers, although simple, leads to environmental, health, and safety issues due to the toxic solvents used to make monomer slurries.

In the prior art, aerogels show the most promise for commercial use. Aerogels are typically formed by supercritical drying of the solvent but this step has been recently shown to be unnecessary. Rather, a surface modifier (e.g., trimethylchlorosilane) is used to prevent further reaction of the gelling agent so that full solvent exchange can be completed and the gel dried with minimal shrinkage due to densification. Because the dielectric constant is nearly proportional to the bulk density of the aerogels, films with dielectric constants as low as 1.1 have been reported. However, there are still questions as to whether aerogels can be easily and economically processed and if they are reliable. For example, infiltration and reaction with water leads to decomposition and breakdown of the aerogel. More specifically, the poor adhesion to the substrate and the high permeability to gas absorption are of chief concern.

The present invention is of porous, low-dielectric-constant films (and methods of manufacture) that do not present the disadvantages of polymers and aerogels when used as an ILD. The embodiments are: (1) agglomerated particles with a deposit within and on top of the layer of agglomerated particles; and (2) hollow and/or porous particles with a deposit within and on top of the layer of hollow and/or porous particles.

The following patents are representative of those using hollow particles in a glass, ceramic, or organic film: U.S. Patent No. Re34,887, to Ushifusa et al.; U.S. Patent No. 5,346,751, to Lau et al.; U.S. Patent No. 5,213,878, to Moh et al.; U.S. Patent No. 5,178,934, to Kellerman; U.S. Patent No. 5,126,192, to Chellis et al.; U.S. Patent No. 5,108,958, to Moh et al.; U.S. Patent No. 4,994,302, to Kellerman; U.S. Patent No. 4,865,875, to Kellerman; U.S. Patent No. 4,781,968, to Kellerman; and U.S. Patent No. 4,141,055, to Berry et al.

The following patents are representative of those disclosing porous aerogel or gel-like films: U.S. Patent No. 5,548,159, to Jeng; U.S. Patent No. 5,525,857, to Gnade et al.; U.S. Patent No. 5,494,858, to Gnade et al.; U.S. Patent No. 5,488,015, to Havemann et al.; U.S. Patent No. 5,472,913, to Havemann et al.; and U.S. Patent No. 5,470,802, to Gnade et al.

SUMMARY OF THE INVENTION (DISCLOSURE OF THE INVENTION)

The present invention is of a film having a dielectric constant of less than 3 and comprising a layer of particles and a deposit within and on top of the particle layer. In the preferred embodiment, the film is low density and has a dielectric constant of less than 2. The particles are agglomerated particles, hollow particles, or porous particles, or combinations thereof. The film is preferably impermeable to gases, and the particles are a metal oxide such as silica, F-doped silica, or hydrogen silsesquioxane. The particles may also be an inorganic material or an organic polymer such as one of the following: polyimides, polyimide siloxanes, fluoropolyimides, fluoropolymers, polysiloxanes, polyurethanes, epoxies, phenoxies, silicones, fluorocarbons, polyxylylenes, polyesters, polyvinyls, polystyrenes, acrylics, diallylphthalates, polyamides, phenolics, polysulfides, polysilsesquioxanes, benzocyclobutenes, parylenes, fiourinated polyimides, poly-naphthalenes, amorphous teflon, and polymer foams. The particles may be coated or composite (such as organic/organic, organic/inorganic, inorganic/inorganic, fluorinated silica/non-fluorinated silica, or silica/non-silica, or combinations thereof). The deposit is similarly selected. The particles and the deposit may be in a combination such as organic polymeric particles and organic polymeric deposit; inorganic particles and organic polymeric deposit; organic polymeric particles and inorganic deposit; and inorganic particles and inorganic deposit. If the particles are agglomerated, they preferably have primary particle sizes between approximately 1 nm and approximately 100 nm, most preferably between approximately 5 nm and approximately 30 nm, resulting in a preferred film thickness of between approximately 5 nm and approximately 1 mm and between approximately 50 nm and approximately 500 nm, respectively. If the particles are hollow and/or porous, the primary particles sizes are preferably between approximately 50 nm and approximately 100 μm and most preferably between approximately 200 nm and approximately 10 μm, resulting in a preferred film thickness of between approximately 500 nm and approximately 1 mm. (Much thicker layers, however, are useful for, e.g., multi-chip modules.) The deposit is substantially planar at its surface. It may comprise a plurality of layers, which may be of different materials and/or morphologies. The deposit may be non-uniformly distributed throughout its depth, including with a concentration lowest in the interior of the particle layer or highest at the surface of the film. The films porosity may have a gradient, such as a lower porosity at the surface of the film and a higher porosity adjacent to the

substrate. Similarly, the permeability of the film may have a gradient, such as a highest permeability in the interior of the particle layer. The particles may be of a plurality of materials. The film may have a characteristic(s) such as uniform microstructure; non-uniform microstructure; narrow particle size distribution; broad particle size distribution; and multi-modal particle size distribution. The film may have a plurality of particle layers and a plurality of deposits, such as a first particle layer, then a deposit layer, a second particle layer (same or different materials / morphologies), and a second deposit layer (same or different materials / morphologies).

The invention is also of a method for making a film, comprising: coating a substrate with particles; drying the particles to form a substantially uniform particle layer; and depositing a deposit layer onto the particle layer. In the preferred embodiment, the following may be performed: The particles may be plasma surface modified, and the deposit layer may be polished (as by chemical mechanical polishing) to form a substantially planar surface. Preferably, the depositing step results in a deposit layer that is substantially planar. The resulting film preferably has a dielectric constant of less than 3 (most preferably less than 2) and is substantially impermeable to gases. The particles may be gas-phase surface modified using a silylating agent, such as silicon alkoxides, amides, halides, alkyl and aryls and combinations thereof, such as trimethylchlorosilane, trimethyl(dimethylamino)silane, hexamethyldisilazane, and dimethylbis(dimethylamino)silane. Coating preferably employs a metal oxide such as silica or F-doped silica, or an organic polymer. Depositing can employ like materials, but not necessarily that used in the coating step. The particle sizes and resulting film thicknesses are as described in the preceding paragraph. If agglomerates are employed, they may be hard agglomerates. Particles in a colloidal solution may be employed, and a reagent may be added to the colloidal solution to act as a binding material for the particles upon completion of the drying step, and a precursor used in the depositing step may comprise a metal-containing compound that is a precursor to a metal oxide (such as SiO_2) film. The coating may be done, for example, by spin-coating or electrophoresis. Depositing may be done by chemical vapor deposition (e.g., plasma-assisted or low pressure). Permitting sufficient chemical vapor infiltration to occur to bond the particles to the substrate may be employed. Depositing may include providing a volatile organic substance as a precursor and depositing an organic deposit, dissolving a precursor in a liquid and forming therewith a film on a surface of the particle layer, depositing the

deposit layer by interfacial precipitation, or depositing a deposit layer by: filling pores of the particle layer with a reactive liquid; spin coating a solution containing a precursor onto a surface of the substrate, thereby causing deposition of an intermediate which does not infiltrate the particle layer; and heating the intermediate to remove remaining liquid and chemically react to and sinter to densify the surface deposit. The depositing step may also comprise chemical vapor deposition sufficiently rapid to form a deposit layer which does not infiltrate the particle layer, providing a volatile metal-containing substance as a precursor and depositing an inorganic deposit, providing a silica-containing substance as a precursor (such as TEOS (tetraethyl orthosilicate) and water; TEOS and alcohol; TEOS and ozone; TMOS (tetramethoxy orthosilicate) and water; TMOS and alcohol; TMOS and ozone; silane and water; silane and ozone; and substituted silanes) and depositing silica, or employing a reactant or reactants selected from the group consisting of TEOS and t-butanol. The particles may be gas-phase modified using a silylating agent. The surface of the film may by liquid-phase surface modified, as by heating the film in water vapor so as to maximize formation of hydroxyl groups on a surface of the film and additionally comprising the subsequent step of silylating the film with a silylating agent.

The invention is further of a film manufactured according to the above method. The film may be formed on a flat surface or a non-flat surface such as one with trenches, vias, contact holes, plugs, and steps.

The invention is additionally of a device comprising a film manufactured according to the method. The device may comprise a layer comprising the film. The layer is preferably an interlayer dielectric material or an intermetal dielectric material. The device may be one or more of the following: energy storage devices; charge separation devices; waveguides; lenses; fiber optics; thermal insulation; glass coatings; integrated circuits; devices incorporating an integrated circuit; flat panel display circuitry; field emission displays; powder electroluminescent displays; electrical insulation; and thermal barrier layers.

A primary object of the present invention is to provide ILD and IMD (intermetal dielectric materials having a dielectric constant less than 3, most preferably less than 2.

Another object of the invention is to provide ILD and IMD materials compatible with both existing and likely future equipment, processes, metallization materials, and barrier or nucleation/adhesion materials.

An advantage of the present invention is that, in certain embodiments, films may be formed at low temperature and ambient pressure.

Another advantage of the present invention is that the materials used, SiO_2 and F-doped SiO_2, are well-understood and acceptable ILD and IMD materials.

An additional advantage of the present invention is that with 80% porosity a dielectric constant of less than 1.8 can be achieved.

Yet another advantage of the present invention is that the films may be made to be impermeable to gas absorption.

Still another advantage of the present invention is that thicknesses of less than 200 nm as well as much thicker films are possible.

Other objects, advantages and novel features, and further scope of applicability of the present invention will be set forth in part in the detailed description to follow, taken in conjunction with the accompanying drawings, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated into and form a part of the specification, illustrate several embodiments of the present invention and, together with the description, serve to explain the principles of the invention. The drawings are only for the purpose of illustrating a preferred embodiment of the invention and are not to be construed as limiting the invention. In the drawings:

Fig. 1 illustrates types of low-dielectric-constant materials for interlayer dielectric films (K is the dielectric constant);

Fig. 2 is a cross-section view of a typical prior-art logic device with four levels of metallization;

Fig. 3 is a cross-section schematic of the microstructure of a porous film made using the hollow and/or porous particle embodiment of the invention (dark areas are the SiO_2 CVD (chemical vapor deposition) layer);

Figs. 4(a) and (b) are scanning electron micrographs of the embodiment of Fig. 3;

Fig. 5 illustrates the preferred four-step process of making the embodiment of Fig. 3;

Figs. 6(a) and (b) are cross-section schematics of the microstructure of a 200 nm porous film (to scale) made using hard agglomerates with primary particle sizes of 25 nm (a) and 10 nm (b) (dark areas are the SiO_2 CVD layer);

Figs. 7(a) and (b) are scanning electron micrographs of the embodiment of Figs. 6(a) (b) with porosities of 78% and calculated dielectric constant of 1.7; note that the film is highly porous near the substrate but dense at the film surface; and

Fig. 8 illustrates the preferred four-step process of making the embodiment of Figs. 6(a) and (b).

DESCRIPTION OF THE PREFERRED EMBODIMENTS (BEST MODES FOR CARRYING OUT THE INVENTION)

The present invention is of low-dielectric-constant (<3, most preferably <2) materials for use particularly in ILD (interlayer dielectric) and IMD (intermetal dielectric) materials. There are two principal embodiments, which will be discussed in order. The first embodiment is of hollow and/or porous particles with a deposit within and on top of the particle layer. The second embodiment is of agglomerated particles with a deposit within and on top of the particle layer.

The first embodiment is a porous silica film **70** comprising hollow and/or porous silica particles **72** impregnated and overcoated by a silica layer **74** (Fig. 3). (Other particle and impregnation/overcoat materials may be substituted, but silica is preferred.) The particles are randomly packed and the interstices yield enough additional porosity along with the porosity already incorporated inside the hollow and/or porous particles to provide a dielectric constant of less than 2 to the film. Preferably, the particles stick to the substrate interface due to chemical and/or

mechanical bonding by a deposited layer, such as one deposited by CVD (chemical vapor deposition). The terms "deposit", "deposition", and the like, as used throughout the specification and claims, are intended to cover any form of deposition, such as CVD, physical vapor deposition (PVD), sputtering, interfacial precipitation, and other methods of depositing materials. Alternatively, a liquid soluble phase additive can be included with the particles so that upon heat treatment or pressure the additive will decompose/densify and form a glue or adhesive layer which will aid in the adhesion (this term also includes absorption and adsorption) and mechanical strength of the particle layer. The film is essentially impervious to gas absorption because the porosity can be isolated below the top surface, with the top surface being overcoated to form a dense barrier. The thickness of the film preferably varies between 0.1 to 10 µm. Figs. 4(a) and (b) show a cross-section of a bed of hollow particles overcoated by a dense film.

The process to produce the hollow and/or porous particle porous film of the invention preferably employs four steps (Fig. 5). Each step may be implemented using standard equipment and existing materials. In the first step, spin-coating is preferably used (electrophoresis from a gas or a liquid or other application methods may also be employed) to apply a bed/layer of hollow and/or porous particles on a substrate. In addition, a liquid phase addition (e.g., tetraethylorthosilicate) can be included in the particle solution which forms a glue or adhesive material upon decomposition/densification, which can aid in the adhesion of the particles to the substrate and the mechanical strength of the layer. Next, this wet particulate layer is dried using a heat lamp or a dry box or other means. The resultant layer has the appearance of particles spread over the substrate to create a porous particulate layer. Next, a deposition process such as CVD (e.g., plasma, low pressure, high pressure, high temperature, low temperature, hot wall, cold wall, and the like) is used to deposit a silica layer onto the surfaces of the particles in the porous layer. Low pressure CVD is the preferred process. Some of the CVD precursor diffuses to the interface between the particles and the substrate and deposits a silica layer that bonds the particles to the substrate and to each other. The reactant for CVD of SiO_2 (or other material) has a sufficiently low reaction efficiency that allows relatively uniform coating of the particles until a certain desired point in time at which the deposition rate can be dramatically increased resulting in reaction of the precursor at the surface of the layer to form a continuous dense coating at the surface of the film.

The surface of the deposited layer may be rough because of the conformal coverage of the particles by the CVD process. If so, it may be desirable as a final step (which is optional) to planarize the film using CMP (chemical mechanical polishing) or other means to provide a flat surface for subsequent processing steps in the fabrication of an integrated circuit. However, it is preferred that the deposited layer be deposited such that it is substantially planar without polishing.

The second embodiment of the invention is a porous silica film **80** comprising hard silica particle agglomerates **82** impregnated and overcoated by a continuous silica layer **84** (Figs. 6(a) and (b)). (Other particle and impregnation/overcoat materials may be substituted, but silica is preferred.) The term "agglomerate" is intended to include multiple particles bonded or held together chemically or mechanically. The primary particles are sufficiently separated because of the three-dimensional nature of the hard agglomerates to yield enough porosity to provide a dielectric constant of less than 3 after impregnation, and most preferably less than 2. The particles will stick to the substrate interface due to chemical and/or mechanical bonding by the low pressure CVD (or other deposition method) layer. Alternatively, a liquid phase additive can be included with the particles so that upon heat treatment the additive will decompose/densify to form a glue or adhesive layer which will aid in the adhesion and mechanical strength of the particle layer. The film is essentially impervious to gas absorption because the porosity can be isolated and the surface can be sufficiently overcoated. The thickness of the film preferably varies between 50 to 500 nm and the primary particle size of the agglomerates preferably varies between 5 to 30 nm. Figs. 7(a) and (b) show a cross-section of a bed of particles with a dense film covering the outer surface.

The preferred process to make the agglomerate film employs four steps (Fig. 8). Each step may be implemented using standard equipment and existing materials. In the first step, spincoating is used (or electrophoresis or other application method) to apply a uniform layer of hard agglomerates of SiO_2 particles on a substrate. In addition, a liquid phase addition (e.g., tetraethylorthosilicate) can be included in the particle solution which forms a glue or adhesive material upon decomposition/ densification, which can aid in the adhesion of the particles to the substrate and the mechanical strength of the layer. Next, this wet particulate layer is dried using a heat lamp or a dry box or other means. The resultant layer has the appearance of silica particles uniformly spread over the substrate to create a porous particulate layer. Next, low pressure CVD

(or other deposition process) is used to deposit a silica layer onto the surfaces of the particles in the porous layer. Some of the CVD precursor diffuses to the interface between the particles and the substrate and deposits a silica layer that bonds the particles to the substrate and to each other. The reactant for CVD of SiO_2 has a sufficiently low reaction efficiency that allows penetration of the reactant into the film, thereby providing a relatively uniform coating of the particles until a certain desired point in time at which the deposition rate can be dramatically increased resulting in reaction of the precursor at the surface of the layer to form a continuous dense coating at the surface of the film. The surface of the deposited layer may be rough because of the conformal coverage of the particles by the CVD process. If so, as an option, a final step may be employed to planarize the film using CIVIP or other means to provide a flat surface for subsequent processing steps in the fabrication of an integrated circuit.

The following discussion refers to options available in both of the above embodiments:

Low pressure CVD is the preferred deposit deposition process because it maximizes chemical vapor infiltration (CVI) to the substrate, which bonds the particles to the substrate. Two reactants are preferably employed, a silica source (e.g., TEOS) and a hydration source (e.g., t-butanol), which allows control of heterogenous reactions and minimization of homogenous reactions. The following additional considerations permit design of a wide variety of useful film types: Deposition of the deposit at high rates using a more reactive precursor provides dense coating at the surface of the film with little deposition in the interior of the film. Deposition of the deposit at low rates using a relatively unreactive precursor provides a relatively uniform deposit throughout the film. A thicker bed of particles results in a dense coating at the surface of the film with little deposition in the interior of the film. A thinner bed of particles favors a more uniform deposit throughout the film. A higher temperature of deposition favors a dense coating at the surface of the film with little deposition in the interior of the film. Lower temperatures favor a more uniform deposit throughout the film. By varying temperatures during the deposition process, the deposit can have varied layers with varying uniformity. Also, by varying the temperature of the substrate, a temperature gradient through the particle layer can be formed. Larger particles in the bed favor a more uniform deposition throughout the film, while smaller particles favor a dense coating at the surface of the film with little deposition in the interior of the film. Particles with more

porosity or greater hollowness favor a film with higher porosity and a lower dielectric constant. Particles that are less densely agglomerated (i.e., have a larger aerodynamic diameter compared to mass diameter) favor a more porous film and a lower dielectric constant.

It is important to emphasize that a controlled amount of infiltration is necessary to sufficiently coat and bond the particles to the underlying substrate and to each other. Fortunately, the porous nature of the particulate layer causes it to have a low thermal conductivity which results in a gradient in temperature when the substrate is heated in a cold wall reactor. Where heating is performed from the back (i.e., through the substrate), the temperature is highest at the interface between the particles and the substrate and lowest at the surface of the particulate layer. This is advantageous to allow sufficient diffusion of the reactant gases to the interface before depletion due to chemical reaction during the early stage of chemical vapor infiltration (CVI) of the deposit into the porous layer. After achieving sufficient deposition at the interface between the particles and the substrate to create a strong chemical/mechanical bond, the temperature gradient can be diminished by heating the substrate and particulate layer uniformly so that rate of reaction is high resulting in deposition of silica primarily at the surface of the particulate layer. As a result, the pores inside the porous film become inaccessible to permeation and diffusion of gases through the surface of the particulate layer thus creating a film with "trapped porosity", "closed porosity", or "isolated porosity".

Parameters such as temperature, pressure, and reactant concentration are adjusted to control the rate of reaction of the reactant so that both the level and location of porosity in the porous film can be varied/optimized. For example, the rate of reaction can be initially slow to produce nearly uniform reaction throughout the particulate layer. This is advantageous to allow sufficient diffusion of the reactant gases to the interface before depletion due to chemical reaction during the early stage of CVI of silica into the porous layer. After completion of a sufficient amount of CVI, the rate of reaction can be increased so that deposition occurs primarily at the surface of the particulate layer. As a result, the pores inside the porous film become inaccessible to permeation and diffusion of gases through the surface of the particulate layer thus creating a film with "trapped porosity", "closed porosity", or "isolated porosity".

The deposit layer may be formed by "interfacial precipitation", which is performed as follows: A solution (using, for example, an alcohol such as ethanol as a solvent) of a precursor to a metal

oxide such as $Si(OEt)_4$, is spin coated onto the particle bed and allowed to infiltrate. This treatment, without further chemical treatment or heating, can be sufficient to adhere the particles to the substrate. If necessary, the particle bed can be heated or reacted with water vapor to increase the extent of reaction of the metal oxide precursor. The solvent/solution is removed from the particle bed by evaporation. (The adhesion of the particles to the substrate can also be achieved by CVD as described previously.) The particle bed is then infiltrated with a solution containing a reagent such as an aqueous (solvent) solution of ammonium hydroxide (reagent). This can be achieved by dropping the solution onto the particle bed placed on a spin coater. Then a solution of a precursor to a metal oxide (e.g., an alcohol (preferably ethanol) solution of $Si(OEt)_4$), where the precursor and reagent are chosen to undergo rapid reaction when they are in contact, is dropped onto the particle bed filled with the reagent solution (e.g., by spin coating). As the two fluids mix, an immediate reaction takes place which causes particle formation on the surface of the particle bed (rather then particle formation inside the particle bed because the interfacial reaction is so rapid). Under certain circumstances, particle formation within the particle layer may occur. For the case of an ammonia solution and a solution containing $Si(OEt)_4$ as precursor, a metal hydroxide or oxy-hydroxide will be precipitated. Depositing this layer by spin-coating helps ensure that the surface precipitated deposit has a high degree of planarity. At this stage, this layer is also likely to be porous. The whole substrate is then heated (e.g., to 100°C) carefully (slowly) to remove (by evaporation through the porous particle deposit layer) the solution contained within the particle bed. The whole article is then heated (preferably to approximately 400°C) to convert the metal hydroxide or oxy-hydroxide layer to metal oxide, and to densify it. This step is not always necessary. Alternatively, the porous deposit may be sealed by CVD of a metal oxide. Accordingly, for purposes of the specification and claims, "interfacial precipitation" means a mixing of two fluids such that a chemical reaction deposits material as the fluids mix.

"Plasma surface modification" may be employed to modify the surface of materials by mass transport of material either in the vapor phase or by surface diffusion. Preferably between the steps of coating the substrate with particles and depositing the deposit, a plasma can be used to modify the surface of the particles. Sufficient exposure to a plasma can provide the necessary amount of redistribution of material to cause the particles to become affixed to the surface of the substrate and

to one another without diminishing the amount of porosity. The plasma can be made especially intense near the end of the surface modification to cause the particles at the surface of the particle layer to become fused and densified together so that the surface is impermeable to gas permeation. It is expected that all plasma atmospheres will perform acceptably but an oxygen atmosphere is preferred because it will cause enhancement of surface diffusion by the control of oxygen vacancies in the silica material. Also, precursors for the deposit can be added to the plasma to result in plasma-enhanced CVD/CVI. Accordingly, for purposes of the specification and claims, "plasma surface modification" means exposing particles to a plasma whereby redistribution of matter occurs and the particles adhere to one another and/or adjacent substances.

Particularly where silica particles are employed, they can benefit from gas-phase surface modification using silylating agents either before or after deposition to provide hydrophobic surfaces with low moisture absorption, providing better characteristics such as less moisture uptake and outgassing when heated. Especially when performed after deposition, selectivity and adhesion for deposition of metals and other materials onto the surface may be modified. Liquid-phase surface modification may also be performed. The additional process step of heating the film in water vapor to form a surface with a high concentration of hydroxyl groups for surface modification by reaction with silylating agents may also be employed. The preferred silylating agents are silicon alkoxides, amides, halides, alkyl and aryls and combinations thereof, such as trimethylchlorosilane, trimethyl(dimethylamino)silane, hexamethyldisilazane, and dimethylbis(dimethylamino)silane.

Industrial Applicability:

The invention is further illustrated by the following additional non-limiting examples.

Example 1 -- Agglomerated Particles

Porous films were made consisting of agglomerated particles overcoated by a deposit of TiO_2. The resultant film can be varied between 200 to 1000 nm and has a porosity that can be varied between 60% to 90% porosity based on the weight of the film. A calculated dielectric constant between 2.2 to 1.3 can be achieved if both the deposit and the particles are silica. Films that had thicknesses less than 300 nm showed strong adhesion to the substrate because they

withstood the peeling of tape off the surface of the film. The roughness of the surface was found to vary in the tens of nanometers range. The films were made according to the following method:

1) Spin-coat agglomerated particles at speeds ranging from 3000 to 10,000 rpm. The particles comprised silica and were dispersed as a colloid in water. A solution concentration of at least 4 wt% was found to give uniform particle layers. The particle layer was spin-coated onto 1 " x 1 " x 1 mm glass substrates.

2) Dry the as-made particle layers in a dry box at 150°C for 30 minutes.

3) Deposit a TiO_2 deposit onto the surfaces of the bed of particles using aerosol-assisted CVD. A solution of 5 wt% titanium tetraisopropoxide (TTIP) in toluene was atomized into droplets, delivered through a preheat zone at 120°C to evaporate the solvent and volatilize the TTIP, and finally chemically reacted into and onto the surfaces of the particles in the layer at a temperature ranging from 325°C to 350°C.

Example 2 -- Agglomerated Particles with the addition of TEOS to the colloid

Porous films were made consisting of agglomerated particles overcoated by a deposit of TiO_2 similar to that of Example 1 except that a silica-containing precursor was added to the colloidal solution of agglomerated particles and water. The silica-containing precursor was decomposed into a hard silica layer which acts as a strong bond between the particles and between the particles and the substrate. Colloidal solutions containing 25 wt% TEOS allowed for sufficient bonding to prevent particles from being removed in a tape test. The films were made according to the following method:

1) Add 25 wt% TEOS to a colloidal solution containing at least 4 wt% agglomerated silica particles. Then spin-coat following step (1) in Example 1.

2) Heat the particle layer in a box furnace at 400°C for 30 minutes to decompose the TEOS into silica.

3) Follow the deposition procedure (step 3) in Example 1.

Example 3 -- Hollow Particles

Porous films were made consisting of hollow particles overcoated by a deposit of TiO_2 similar to that of Example 1. A solution containing 7 wt% hollow alumina particles in water was used. The

average size of the particles was 3 μm. The film thickness varied from 4 to 5 μm. Porosity was found both inside the particles and between the particles.

Example 4 -- Industrial Applicability

The present invention is useful in the following fields / applications:

- Energy storage devices including supercapacitors and ultracapacitors;
- Charge separation (capacitors in general);
- Waveguides, lenses, fiber optics;
- Thermal insulation (e.g., between two areas that get hot in an electronic device);
- Glass coatings (e.g., to control optical or thermal characteristics);
- Integrated circuits;
- Multichip modules;
- Devices that incorporate an integrated circuit;
- Flat panel display circuitry;
- Field emission displays (e.g., used as an electrical insulation barrier);
- Powder electroluminescent displays;
- Electrical insulation;
- Barrier to protect low melting materials from high heat; thermal barrier layer;
- Barrier to keep things cold such as cryo-related devices;
- Electrical insulation layer for supercapacitors;
- Electrical insulation layer for batteries;
- Electrical insulation layer for multilayer ceramic components; and
- Electrical insulation layer for multilayer ceramic packaging.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

Although the invention has been described in detail with particular reference to these preferred embodiments, other embodiments can achieve the same results. Variations and modifications of the present invention will be obvious to those skilled in the art and it is intended to

cover in the appended claims all such modifications and equivalents. The entire disclosures of all references, applications, patents, and publications cited above are hereby incorporated by reference.

What is claimed is:

1. A film having a dielectric constant of less than 3 and comprising a layer of particles and a deposit within and on top of the particle layer.

2. The film of claim 1 wherein said film comprises a low density film.

3. The film of claim 1 wherein said film has a dielectric constant of less than 2.

4. The film of claim 1 wherein said particles are selected from the group consisting of agglomerated particles, hollow particles, porous particles, and combinations thereof.

5. The film of claim 1 wherein said film is substantially impermeable to gases.

6. The film of claim 1 wherein said particles comprise an inorganic material.

7. The film of claim 6 wherein said particles comprise a metal oxide.

8. The film of claim 7 wherein said particles comprise silica.

9. The film of claim 8 wherein said particles comprise F-doped silica.

10. The film of claim 6 wherein said particles comprise hydrogen silsesquioxane.

11. The film of claim 1 wherein said particles comprise an organic polymer.

12. The film of claim 11 wherein said particles comprise an organic polymer selected from the group consisting of polyimides, polyimide siloxanes, fluoropolyimides, fluoropolymers, polysiloxanes, polyurethanes, epoxies, phenoxies, silicones, fluorocarbons, polyxylylenes, polyesters, polyvinyls, polystyrenes, acrylics, diallylphthalates, polyamides, phenolics, polysulfides, polysilsesquioxanes, benzocyclobutenes, parylenes, fluorinated polyimides, poly-naphthalenes, amorphous teflon, and polymer foams.

13. The film of claim 1 wherein said particles comprise coated particles.

14. The film of claim 1 wherein said particles comprise composite particles.

15. The film of claim 1 wherein said particles comprise composite particles that are composites selected from the group consisting of organic/organic, organic/inorganic, inorganic/inorganic, fluorinated silica/non-fluorinated silica, silica/non-silica, and combinations thereof.

16. The film of claim 1 wherein said deposit comprises an inorganic material.

17. The film of claim 16 wherein said deposit comprises a metal oxide.

18. The film of claim 17 wherein said deposit comprises silica.

19. The film of claim 18 wherein said deposit comprises F-doped silica.

20. The film of claim 16 wherein said deposit comprises hydrogen silsesquioxane.

21. The film of claim 1 wherein said deposit comprises an organic polymer.

22. The film of claim 21 wherein said deposit comprises an organic polymer selected from the group consisting of polyimides, polyimide siloxanes, fluoropolyimides, fluoropolymers, polysiloxanes, polyurethanes, epoxies, phenoxies, silicones, fluorocarbons, polyxylylenes, polyesters, polyvinyls, polystyrenes, acrylics, diallylphthalates, polyamides, phenolics, polysulfides, polysilsesquioxanes, benzocyclobutenes, parylenes, fluorinated polyimides, poly-naphthalenes, amorphous teflon, and polymer foams.

23. The film of claim 1 wherein said particles and said deposit are present in a combination selected from the group consisting of organic polymeric particles and organic polymeric deposit; inorganic particles and organic polymeric deposit; organic polymeric particles and inorganic deposit; and inorganic particles and inorganic deposit.

24. The film of claim 1 wherein said particles are agglomerated particles having primary particle sizes between approximately 1 nm and approximately 100 nm.

25. The film of claim 24 wherein said particles are agglomerated particles having primary particle sizes between approximately 5 nm and approximately 30 nm.

26. The film of claim 1 wherein said film has a thickness of between approximately 5 nm and approximately 1 mm.

27. The film of claim 26 wherein said film has a thickness of between approximately 50 nm and approximately 500 nm.

28. The film of claim 1 wherein said particles are selected from the group consisting of hollow particles and porous particles and combinations thereof having primary particle sizes between approximately 50 nm and approximately 100 μm.

29. The film of claim 28 wherein said particles are selected from the group consisting of hollow particles and porous particles and combinations thereof having primary particle sizes between approximately 200 nm and approximately 10 μm.

30. The film of claim 1 wherein said film has a thickness of between approximately 500 nm and approximately 1 mm.

31. The film of claim 1 wherein said deposit is substantially planar at a surface thereof.

32. The film of claim 1 wherein said deposit comprises a plurality of layers.

33. The film of claim 32 wherein said deposit comprises layers comprising different materials.

34. The film of claim 1 wherein said deposit is non-uniformly distributed throughout its depth.

35. The film of claim 34 wherein said concentration of said deposit is lowest in an interior of said particle layer.

36. The film of claim 34 wherein said concentration of said deposit is highest at a surface of said film.

37. The film of claim 1 wherein said film comprises a gradient in porosity.

38. The film of claim 37 wherein said film comprises a lower porosity at a surface of said film and a higher porosity adjacent to said substrate.

39. The film of claim 1 wherein said film comprises a gradient in permeability;

40. The film of claim 39 wherein said film comprises a highest permeability in an interior of said particle layer.

41. The film of claim 1 wherein said particles comprise a plurality of materials.

42. The film of claim 1 wherein said film comprises a characteristic selected from the group consisting of uniform microstructure; non-uniform microstructure; narrow particle size distribution; broad particle size distribution; and multi-modal particle size distribution.

43. A method for making a film, the method comprising the steps of:

a) coating a substrate with particles;

b) drying the particles to form a substantially uniform particle layer; and

c) depositing a deposit layer onto the particle layer.

44. The method of claim 43 additionally comprising the step of plasma surface modifying the particles.

45. The method of claim 43 additionally comprising the step of polishing the deposit layer to form a substantially planar surface.

46. The method of claim 45 wherein the polishing step comprises chemical mechanical polishing.

47. The method of claim 43 wherein the depositing step results in a deposit layer that is substantially planar.

48. The method of claim 43 wherein the resulting film has a dielectric constant of less than 3.

49. The method of claim 48 wherein the resulting film has a dielectric constant of less than 2.

50. The method of claim 43 wherein the resulting film is substantially impermeable to gases.

51. The method of claim 43 additionally comprising gas-phase surface modifying the particles using a silylating agent.

52. The method of claim 51 wherein the modifying step comprises using a silylating agent selected from the group consisting of silicon alkoxides, amides, halides, alkyl and aryls and combinations thereof.

53. The method of claim 52 wherein the modifying step comprises using a silylating agent selected from the group consisting of trimethylchlorosilane, trimethyl(dimethylamino)silane, hexamethyldisilazane, and dimethylbis(dimethylamino)silane.

54. The method of claim 43 wherein the coating step comprises coating with a metal oxide.

55. The method of claim 54 wherein the coating step comprises coating with silica.

56. The method of claim 55 wherein the coating step comprises coating with F-doped silica.

57. The method of claim 43 wherein the coating step comprises coating with an organic polymer.

58. The method of claim 43 wherein the depositing step comprises depositing a metal oxide layer.

59. The method of claim 58 wherein the depositing step comprises depositing a silica layer.

60. The method of claim 59 wherein the depositing step comprises depositing an F-doped silica layer.

61. The method of claim 43 wherein the depositing step comprises depositing a organic polymer.

62. The method of claim 43 wherein the coating step comprises coating with agglomerated particles having primary particle sizes between approximately 1 nm and approximately 100 nm.

63. The method of claim 62 wherein the coating step comprises coating with agglomerated particles having primary particle sizes between approximately 5 nm and approximately 30 nm.

64. The method of claim 43 wherein the resulting film has a thickness of between approximately 5 nm and approximately 1 mm.

65. The method of claim 64 wherein the resulting film has a thickness of between approximately 50 nm and approximately 500 nm.

66. The method of claim 43 wherein the coating step comprises coating with hard agglomerates.

67. The method of claim 43 wherein the coating step comprises coating with particles selected from the group consisting of hollow particles and porous particles and combinations thereof having primary particle sizes between approximately 50 nm and approximately 100 μm.

68. The method of claim 67 wherein the coating step comprises coating with particle selected from the group consisting of hollow particles and porous particles and combinations thereof having primary particle sizes between approximately 200 nm and approximately 10 μm.

69. The method of claim 43 wherein the resulting film has a thickness of between approximately 500 nm and approximately 1 mm.

70. The method of claim 43 wherein the coating step comprises coating with particles in a colloidal solution.

71. The method of claim 70 additionally comprising the step of adding a reagent to the colloidal solution to act as a binding material for the particles upon completion of the drying step.

72. The method of claim 71 wherein the reagent in the adding step and a precursor used in the depositing step comprise a metal-containing compound that is a precursor to a metal oxide film.

73. The method of claim 72 wherein the reagent in the adding step and a precursor used in the depositing step comprise a metal-containing compound that is a precursor to a SiO_2 film.

74. The method of claim 43 wherein the coating step comprises spin-coating.

75. The method of claim 43 wherein the coating step comprises electrophoresis.

76. The method of claim 43 wherein the depositing step comprises depositing by chemical vapor deposition.

77. The method of claim 76 wherein the depositing step comprises depositing by plasma-assisted chemical vapor deposition.

78. The method of claim 76 wherein the depositing step comprises depositing by low pressure chemical vapor deposition.

79. The method of claim 43 additionally comprising the step of permitting sufficient chemical vapor infiltration to occur to bond the particles to the substrate.

80. The method of claim 43 wherein the depositing step comprises providing a volatile organic substance as a precursor and depositing an organic deposit.

81. The method of claim 43 wherein the depositing step comprises dissolving a precursor in a liquid and forming therewith a film on a surface of the particle layer.

82. The method of claim 43 wherein the depositing step comprises depositing the deposit layer by interfacial precipitation.

83. The method of claim 43 wherein the depositing step comprises depositing a deposit layer by the steps of:

a) filling pores of the particle layer with a reactive liquid;

b) spin coating a solution containing a precursor onto a surface of the substrate, thereby causing deposition of an intermediate which does not infiltrate the particle layer; and

c) heating the intermediate to remove remaining liquid and densify the surface deposit.

84. The method of claim 43 wherein the depositing step comprises depositing a deposit layer by chemical vapor deposition sufficiently rapid to form a deposit layer which does not infiltrate the particle layer.

85. The method of claim 43 wherein the depositing step comprises providing a metal-containing substance as a precursor and depositing an inorganic deposit.

86. The method of claim 43 wherein the depositing step comprises providing a silica-containing substance as a precursor and depositing silica.

87. The method of claim 86 wherein the providing step comprises providing matter selected from the group consisting of TEOS and water; TEOS and alcohol; TEOS and ozone; TMOS and water; TMOS and alcohol; TMOS and ozone; silane and water; silane and ozone; and substituted silanes.

88. The method of claim 43 wherein the depositing step comprises employing a reactant or reactants selected from the group consisting of TEOS and t-butanol.

89. The method of claim 43 further comprising the step of gas-phase modifying the particles using a silylating agent.

90. The method of claim 43 further comprising the step of liquid-phase surface modifying a surface of the film.

91. The method of claim 90 further comprising the step of heating the film in water vapor.

92. The method of claim 91 wherein the heating step substantially maximizes formation of hydroxyl groups on a surface of the film and additionally comprising the subsequent step of silylating the film with a silylating agent.

93. A film manufactured according to the method of claim 43.

94. The film of claim 93 wherein said film is formed on a flat surface.

95. The film of claim 93 wherein said film is formed on a surface comprising one or more of the features selected from the group consisting of trenches, vias, contact holes, plugs, and steps.

96. A device comprising a film manufactured according to the method of claim 43.

97. The device of claim 96 wherein said device comprises a layer comprising said film and wherein said layer is selected from the group consisting of interlayer dielectric materials and intermetal dielectric materials.

98. The device of claim 96 wherein said device is selected from the group consisting of energy storage devices; charge separation devices; waveguides; lenses; fiber optics; thermal insulation; glass coatings; integrated circuits; devices incorporating an integrated circuit; flat panel display circuitry; field emission displays; powder electroluminescent displays; electrical insulation; and thermal barrier layers.

99. The film of claim 1 comprising a plurality of particle layers and a plurality of deposits.

100. The method of claim 83 wherein the filling step comprises filling with an aqueous solution selected from the group consisting of acidic solutions and basic solutions.

101. The method of claim 83 wherein the spin coating step causes deposition of a substance selected from the group consisting of metal hydroxides, metal oxides, and oxy-hydroxides.

102. The method of claim 43 additionally comprising the step of creating a temperature gradient in the particle layer.

103. The method of claim 102 wherein the step of creating a temperature gradient comprises heating the particle layer through the substrate.

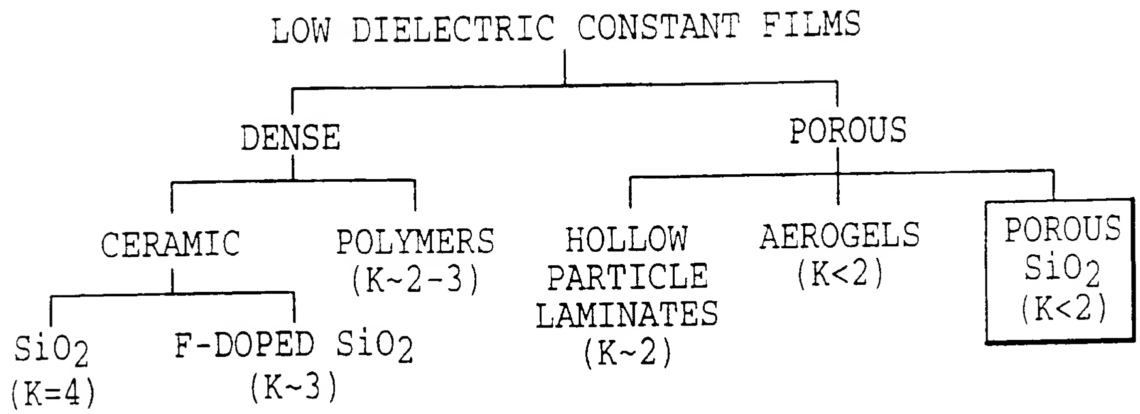
LOW DIELECTRIC CONSTANT FILMS
DENSE
POROUS
CERAMIC
POLYMERS (K~2-3)
HOLLOW PARTICLE LAMINATES (K~2)
AEROGELS (K<2)
POROUS SiO_2 (K<2)
SiO_2 (K=4)
F-DOPED SiO_2 (K~3)

FIG.1

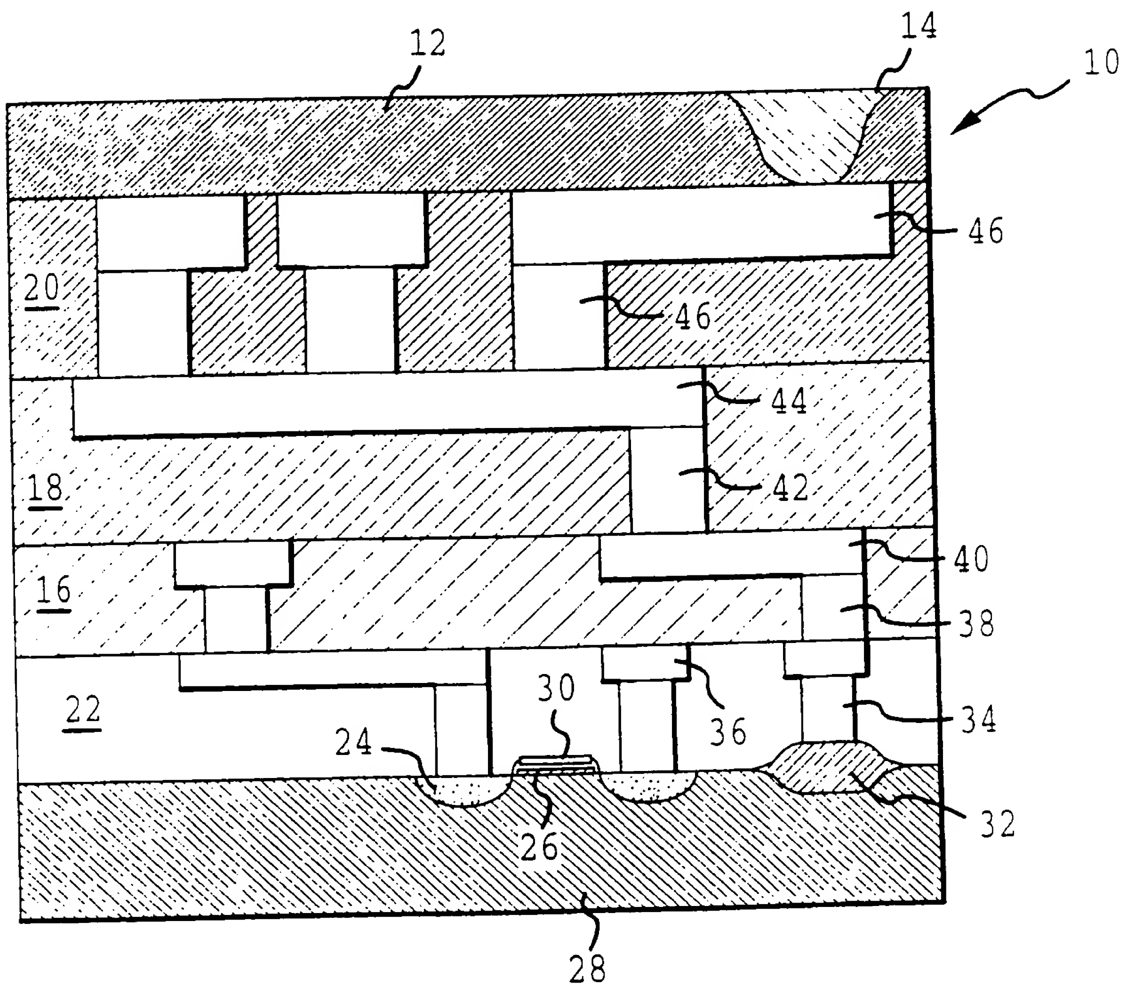
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FIG.2

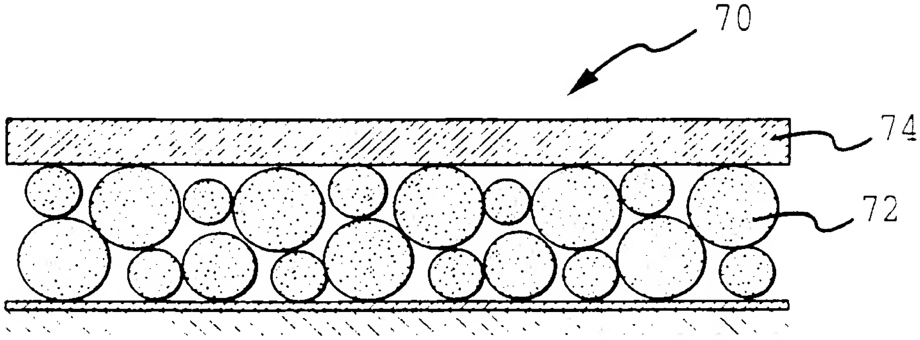

FIG.3

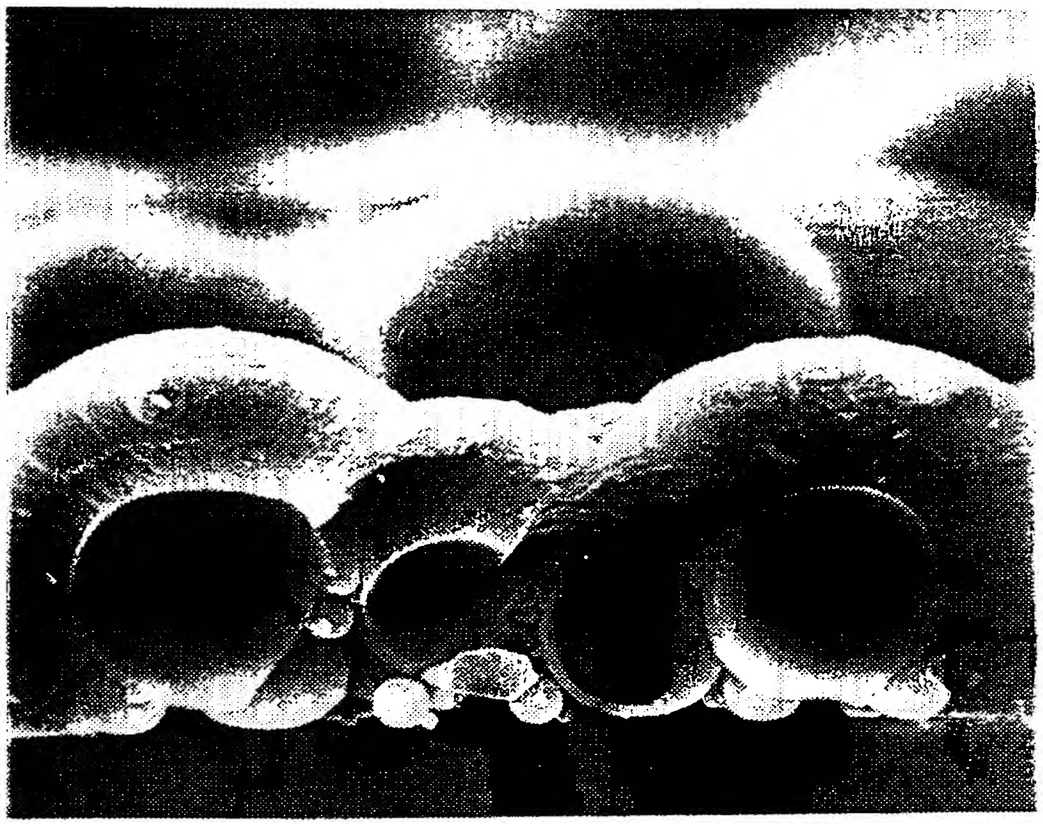

FIG.4(a)

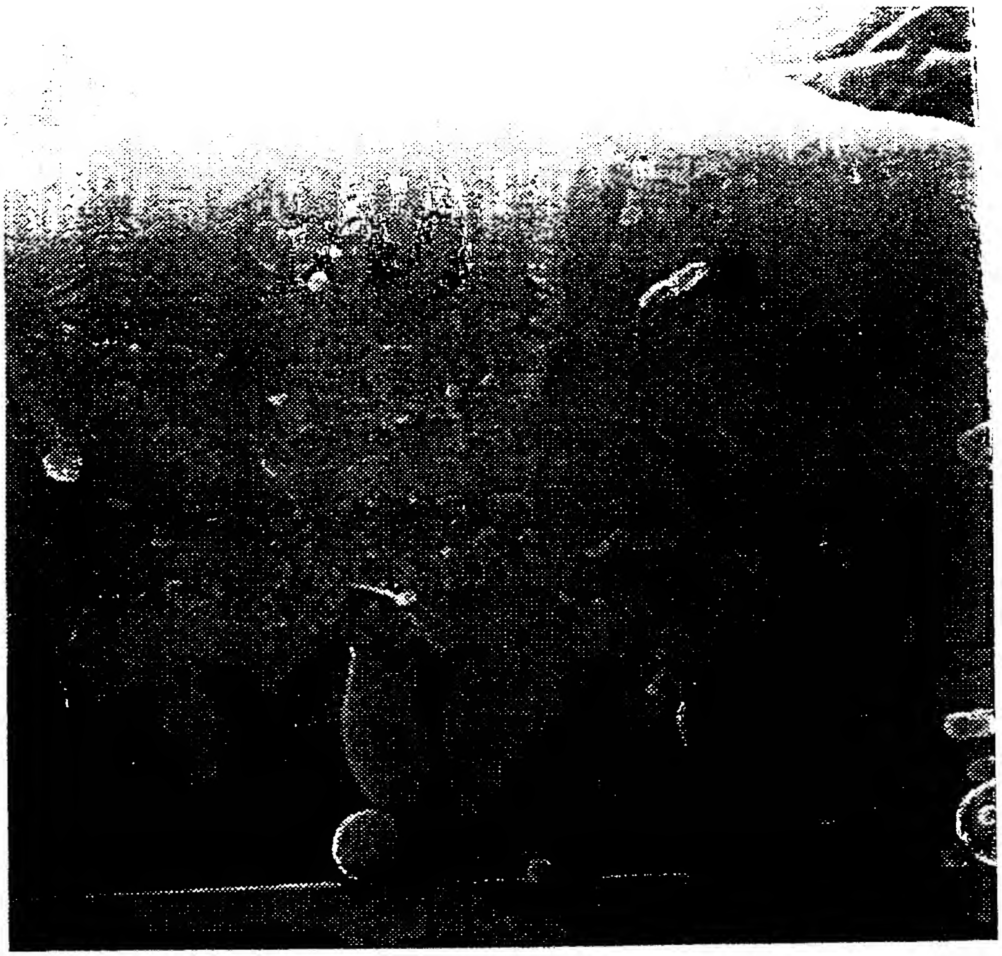

FIG.4(b)

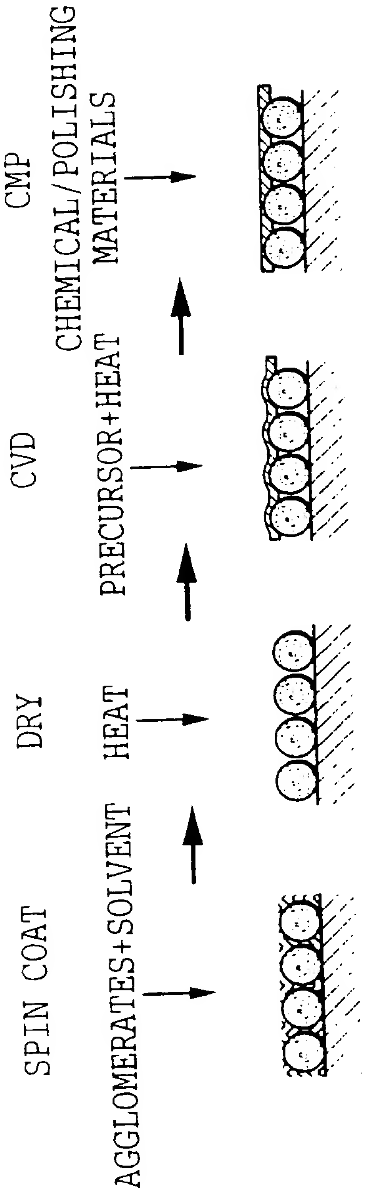

FIG.5

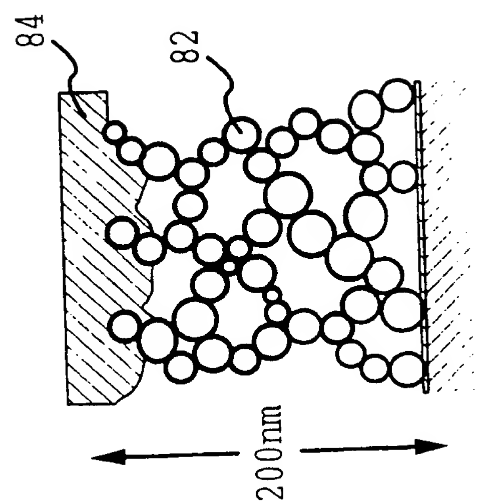

FIG.6(a)

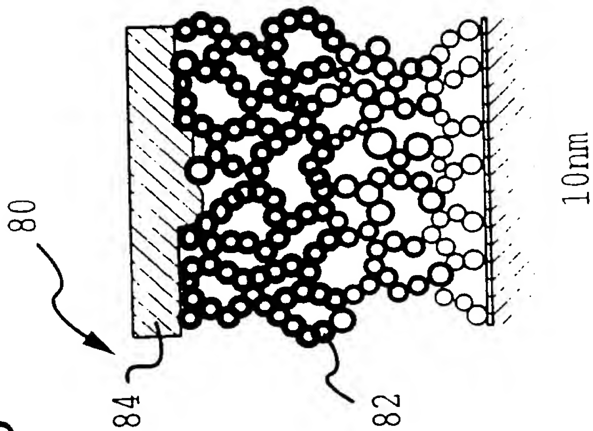

FIG.6(b)

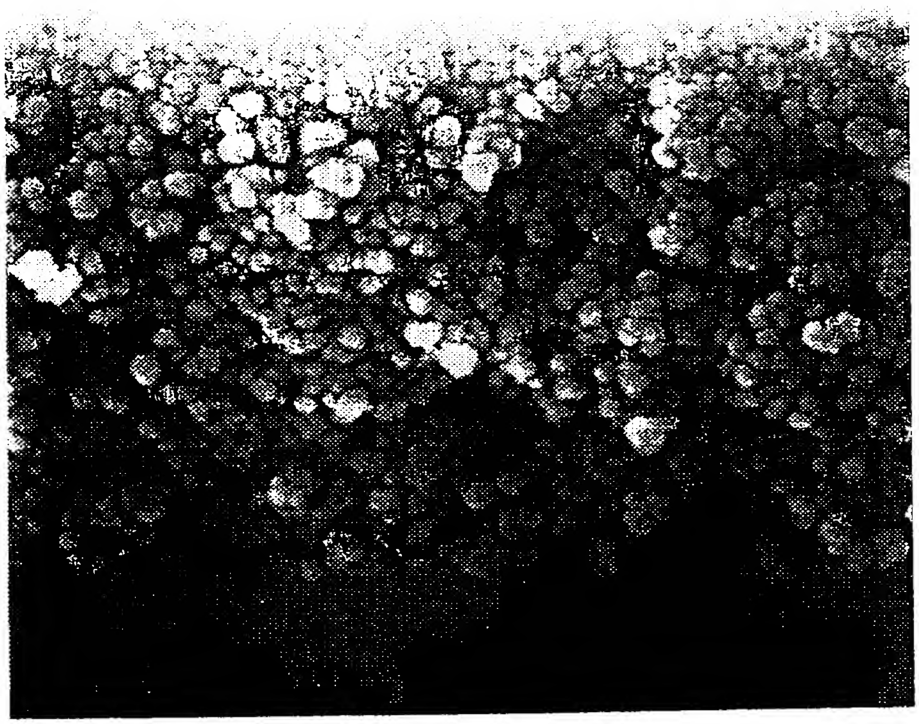

FIG.7(a)

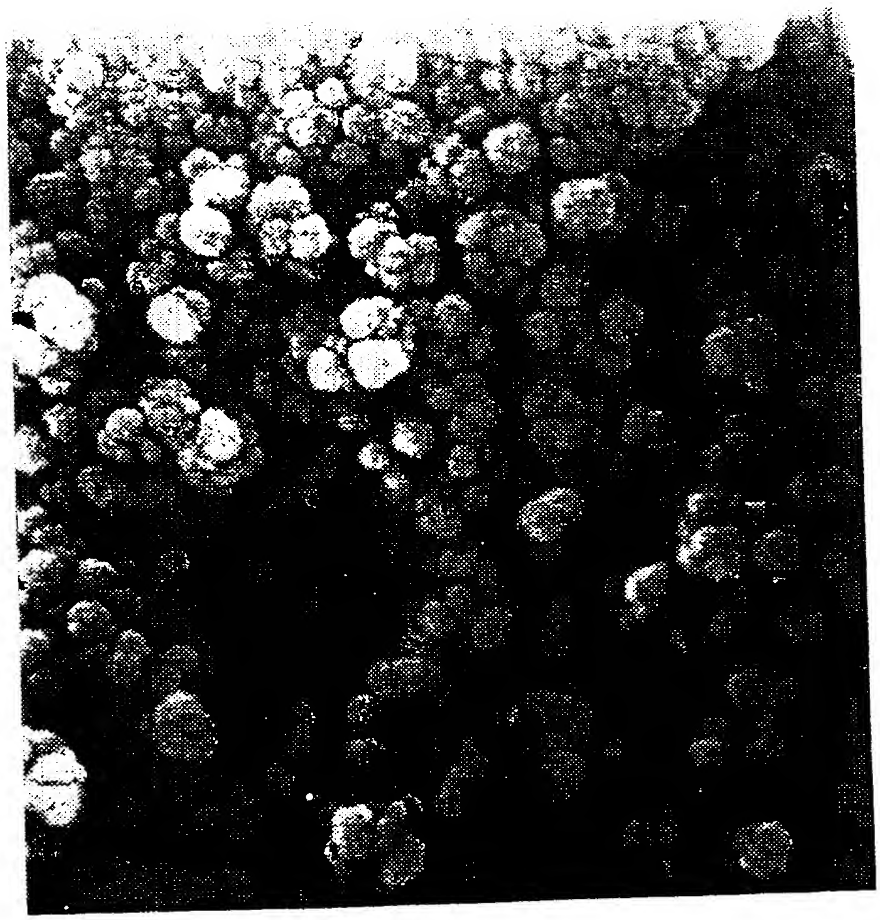

FIG.7(b)

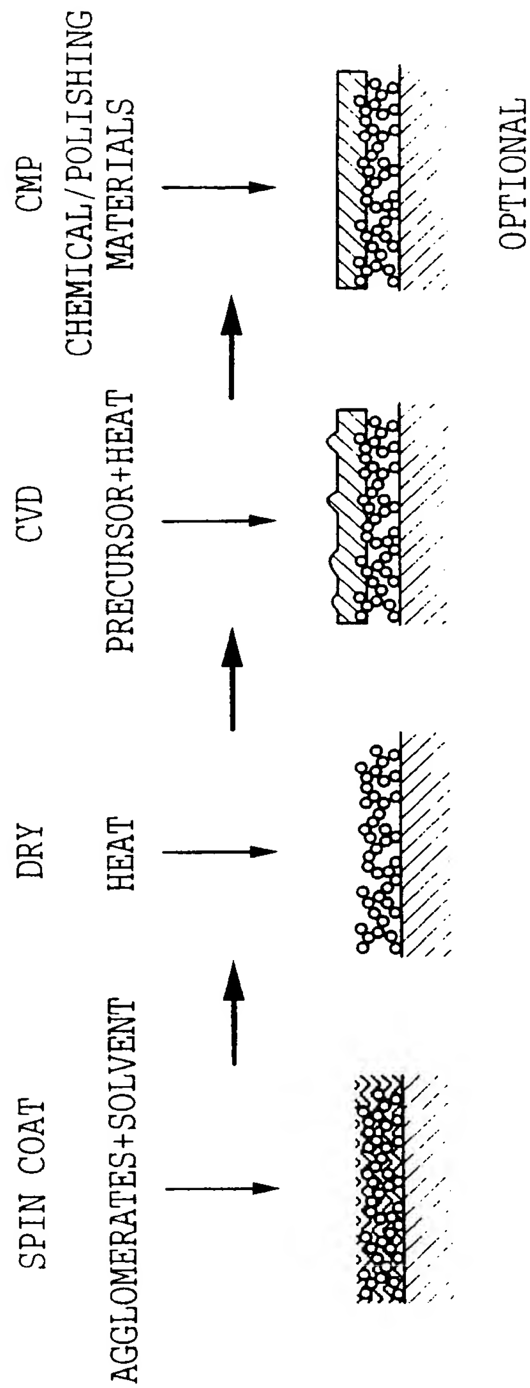
SPIN COAT
AGGLOMERATES+SOLVENT
DRY
HEAT
CVD
PRECURSOR+HEAT
CMP
CHEMICAL/POLISHING
MATERIALS
OPTIONAL

FIG.8

PCT

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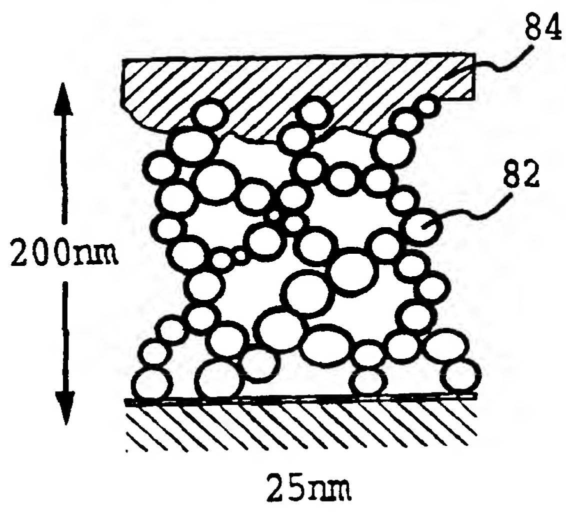
(54) **Title:** LOW DENSITY FILM FOR LOW DIELECTRIC CONSTANT APPLICATIONS

(57) **Abstract**

A film having a dielectric constant of less than 3 (most preferably less than 2) and comprising a layer of particles (82) and a deposit (84) on top of and within the particle layer, and a method of making same. The particles are agglomerated particles, hollow particles, porous particles, or a combination thereof. The film is substantially planar on its surface, and the film is substantially impermeable to gases. The method comprises coating a substrate with the particles (preferably spin-coating a colloidal solution); drying the particles to form a substantially uniform particle layer; depositing a deposit onto the particle layer (preferably by low pressure chemical vapor deposition and causing chemical vapor infiltration to bond the particles to the substrate); and optionally polishing/planarizing the deposit surface (preferably by chemical mechanical polishing).



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INTERNATIONAL SEARCH REPORT

International application No
PCT/US98/09295

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) H01L 21/31
US CL Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 257/ 642, 643, 644; 438/623, 624, 778, 781, 427/96, 189, 204, 214, 148 DIG81, 438/FOR395

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X, E ----- Y, E	US 5,801,092 A (AYERS) 01 September 1998 (01.09.98) Abstract	1 and 43 ---------- 2-42, 44-103
X,E ----- Y,E	US 5,776,828 A (GIVINS) 07 July 1998 (07.07.98) Abstract.	1-3, 43 ---------- 4-42, 44-103
X,E ----- Y,E	US 5,354,611 A (ARTHUR et al.) 11 October 1998, (11.10.98) Abstract and column 3, lines 20-25.	1, 43 -------- 2-42, 44-103
Y	US 5,055,342 A (MARKOVICH et al.) 08 October 1991 (0A8.10.91) Abstract and col. 7, claims 1 and 6.	1-1031-

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
04 DECEMBER 1998	14 JAN 1999

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C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,614,250 A (Diener et al.) 25 March 1997, Abstract, column 3, lines 1-5 and 45-50, and column 10, claim 10	1-103
Y	US 4,865,875 A (Kellerman) 12 September 1989, Abstract and column 6, lines 45-50	1-103
Y	US 4,849,284 A (ARTHUR et al.) 18 July 1989 (18.07.89) Abstract.	1-103
Y	JP 407112126 A (WATAKABE) 02 May 1995 (02.05.95) English Abstract.	1-103
Y	JP 406097298 A (NAGASHIMA) 08 April 1994 (08.04.94), English Abstract.	1-103

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US CL :

257/642, 643, 644; 438/623, 624, 778, 781; 427/96, 189, 204, 214